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Technology

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Extremely Sensitive Carbon Monoxide Indicator Developed by Bureau Chemists

A colorimetric indicating gel that will detect and estimate less than 1 part of carbon monoxide in 500 million parts of air, a sensitivity more than 100 times greater than that attained by former chemical indicators, has recently been announced by the Bureau's Gas Chemistry Section. This gel will also detect 0.001 percent by volume in less than 1 minute, and determine physiologically significant amounts (0.01 to 0.4 percent) in approximately 1 minute at ground level. The indicator is so sensitive that it is possible to diagnose carbon monoxide poisoning by analyzing exhaled air instead of taking a blood sample for analysis. Developed to meet the war-time demand for a simple and sensitive means for determination of very small amounts of carbon monoxide in military equipment and installations, it offers promise for many peacetime applications.

Early in the war it was evident that the determination of physiologically significant amounts of carbon monoxide in aircraft, particularly at high altitudes, would assume increasing importance. This was true as well with such equipment as flame throwers, tanks, gun pits and turrets, PT boats, landing craft, and aircraft carriers.

Existing methods of determining carbon monoxide possess two decided disadvantages. First, the simple and inexpensive, easily available methods were not sufficiently sensitive. Second, those which were sufficiently sensitive were unsuited for field use, with the exception of one expensive instrument, available in limited quantities, whose operation and maintenance was generally beyond the abilities of nontechnical men in the services.

During 1941 the Royal Aircraft Establishment, Farnborough, England, developed an indicator for the detection and estimation of small amounts of carbon monoxide on board aircraft. As this indicator was not entirely satisfactory, the Bureau of Aeronautics, Navy Department, and later the U. S. Army Air Forces requested the National Bureau of Standards to study the RAE gel, with the object of improving it or developing a suitable substitute. Starting with this material, Bureau chemists produced an indicator about four times as sensitive, more adaptable to field conditions, and truly colorimetric.

The indicating material, yellow in color, is a silica gel impregnated with a complex silico-molybdate compound and catalyzed by means of palladium in the form of the sulfate. The yellow indicator turns various shades of green and bluish green on exposure to very low concentrations of carbon monoxide. The color response is a function of time by concentration of carbon monoxide—a direct parallel to the physiological response to this gas. For use, the indicator gel is sealed in a small glass about 5 in. long and the approximate diameter of a lead pencil, with protecting layers of pure silica gel in each end of the tube.

To make a test, the ends of the indicating tube are broken off and the tube inserted in an ordinary 2-oz rubber aspirator bulb equipped with a special rate-controlling valve. The air to be tested is drawn through the tube by squeezing the bulb once and any color that develops is compared with a set of standard color chips. Such a test can be made by untrained personnel in about 1 minute. For use in aircraft, tables giving correction factors for altitude are provided. Complete equipment for field use can be carried in a box which fits the pocket of a field jacket.

The NBS Colorimetric Carbon Monoxide Indicators were made only at the National Bureau of Standards, and altogether more than a half million were supplied for the military services of the United States, Canada, and Great Britain. Patents have been issued on the device and assigned to the Secretary of Commerce.

Among the prospective peacetime uses are examination of air in and around busses, automobiles, garages, furnaces and furnace rooms, industrial plants, and civilian transport planes, and in the diagnosis of carbon monoxide poisoning. The tubes may also be modified to serve as detectors of other reducing gases and vapors, including many organic vapors.

International Electrotechnical Commission Council Resumes Meetings

The International Electrotechnical Commission, which has necessarily been inactive during the war, has

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now taken steps to revive its technical work and also to join with other bodies in forming a comprehensive organization to deal with problems of standardization on an international scale. A meeting of the IEC Council was held in Paris on July 8 and 9, and was attended by delegates from 16 countries—Belgium, Canada, Czechoslovakia, Denmark, France, Great Britain, India, Italy, Netherlands, Norway, Poland, Portugal, Sweden, Switzerland, United States of America, and Union of Soviet Socialist Republics.

The Commission was established in 1906 in pursuance of a resolution adopted by the Chamber of Government Delegates at the International Electrical Congress of St. Louis in 1904, asking the cooperation of the technical societies of the world in standardizing the nomenclature and ratings of electric apparatus and machinery. Except for interruptions by war, the Commission has continued its activities since 1906, and its scope has broadened with the growth of the electrical industry throughout the world. Twenty-six countries were represented in the Commission before the recent war.

The National Bureau of Standards is one of 13 organizations whose representatives constitute the United States National Committee of the Commission; E. C. Crittenden, Associate Director of the Bureau, is President of the National Committee, and represented it at the Council meeting.

The meeting adopted unanimously a resolution favoring affiliation with a proposed new International Standards Association to be formed by a merger of the war-time United Nations Standards Coordinating Committee and the prewar Federation of National Standardizing Associations (commonly called the ISA). Final action by the IEC will be taken after the new general organization has worked out precise details of its constitution and bylaws. There is, however, no reason to doubt that the IEC will operate as the electrical division of the new ISA, retaining its own name and procedures, but gaining the advantages of a common central office that will be a point of contact with various other bodies carrying on related work.

The Council reviewed the status of projects that were under way in 1939, and made plans to push forward those considered most urgently needed. In view of conditions now existing in Europe, the highest urgency was assigned to unification of designs for lamp bases and sockets, and to agreement upon standard voltages for electric power supply. A new, separate committee was set up to recommend standard voltages for transmission lines above 220,000 volts. A special committee including representatives from several other organizations is to continue work on electrical causes of disturbances to radio reception. It is hoped that these committees can work out proposals and prepare documents that will justify international meetings to discuss them within a year. There are also a number of reports that were considered at the 1938 meeting of the Commission, but which required further work not completed before the war. Some of these can be put out now without waiting for meetings. These include letter symbols for electrical quantities and standards for the rating of hydraulic turbines, steam turbines, and internal-combustion engines.

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Bureau Battery Research Reported In Five Papers

Fundamental contributions to the theory of the Leclanche dry cell through X-ray diffraction and electron microscope studies; dry cells for low-temperature applications; a perchloric acid battery, also useful at low temperatures; a plastic coating that protects dry cells in tropical climates by allowing them to "breathe"; and a silver peroxide primary cell, are among the developments in battery research by the Bureau's Electrochemistry Section that were reported to the fall meeting of the Electrochemical Society in Toronto. Five of eleven papers in a symposium on electric batteries, held as a part of the meeting, were presented by members of the Bureau staff.

Many different types of batteries are required for various purposes, and the Bureau has pioneered in the development of several new types to meet some of these specific needs. Each of the five papers deals with a separate phase of the work.

Equilibrium Reactions in the Leclanche Dry Cell Determined by X-Ray and Microscope

Identification of the compounds in the Leclanche dry cell by means of X-ray diffraction methods and the petrographic microscope gives a much clearer picture than ever before of the reactions taking place within the cell. At the same time, certain anomalous results that have been previously observed are explained by the discovery that reactions are entirely different in acid and basic solutions.

Although the Leclanche cell (that is, the familiar dry cell best known in the form of flashlight batteries) was invented over 80 years ago, an adequate explanation of its theory of operation has not been previously worked out. There is no general agreement regarding the essential current-producing reaction or the final reaction products. Recent X-ray and microscopic studies, however, have disclosed many characteristics of the oxides of manganese and the carbon blacks, essential components of the cells.

In this paper, H. F. McMurdie, of the Bureau's Laboratory of Microscopic and Diffraction Analysis, with D. N. Craig and G. W. Vinal, of the Electrochemistry Section, approach the problem in three parts. First, they identify the solid phases formed with a solution similar to a dry-cell electrolyte under equilibrium conditions, but with no manganese compounds present (systems containing ZnO, $ZnCl_2$, NH_4Cl, H_2O).

The second part of the paper deals with manganese oxides and the role of soluble divalent manganese in typical dry-cell electrolytes. When manganese dioxide is reduced in the presence of zinc, a condition existing in the dry cell, the zinc-manganese compound hetaerolite ($ZnO.Mn_2O_3$) is formed. This compound is also identified as a product of discharge in dry cells.

In the third part the pH versus potential relationships of manganese dioxide electrodes are described. The nature of the reactions in acidic and basic solutions is shown to be entirely different, the valence change in the former being two, and in the latter, one. In typical dry-cell electrolytes and over the pH range usually encountered in dry cells, the data indicate that the most important equilibrium reaction is that resulting in the formation of hetaerolite.

Both X-ray and chemical determinations agree in establishing the presence of small amounts of soluble manganese and the character of the oxide crystals at any stage between low and high pH values.

Low-Temperature Dry Cells

Dry cells that perform satisfactorily at temperatures of $-30°$ C. ($-22°$ F.) and lower, and that also possess other essential properties, such as suitable shelf life, are described in a paper by G. W. Vinal, Earl Otto, and C. K. Morehouse.

As early as 1922, Bureau scientists had pointed out that dry cells of the ordinary ammonium chloride type become inoperative at a temperature of about $-20°$ C. ($-4°$ F.). Operations in arctic regions and at high altitudes require a cell that will operate at considerably lower temperatures, and up to 1941, dry cells meeting this requirement were not available in the United States. Accordingly, the Bureau was requested to undertake the development of a low-temperature dry cell.

On the basis of previous unpublished work at the Bureau, a cell was developed by substituting methylamine hydrochloride for ammonium chloride; the electrical characteristics were good, but its shelf life was poor. Further investigation revealed that the addition of a small amount of ammonium chloride caused a stabilization of voltage, amperage, and capacity, and prolonged the shelf life.

Following the Japanese Manchurian campaign in 1931, two Japanese scientists published results of an investigation of calcium chloride-zinc chloride solutions, in which they found that some of these solutions did not freeze even at $-100°$ C. Although they succeeded in producing a battery that would function at low temperatures, it did not prove entirely satisfactory.

Extending this work at the Bureau, it was found that certain formulas had apparently been overlooked. For example, cells in which the mole strength of the zinc chloride is equal to or greater than the calcium chloride show a very constant voltage. Addition of ammonium chloride increases its output.

The calcium chloride-ammonium chloride type of cell has given outstanding performance and, at present, seems to be superior to the methylamine hydrochloride type.

Perchloric Acid Battery Operates at −60° C

A lead dioxide cell with perchloric acid as the electrolyte has been operated successfully at a temperature of −60° C., and this is the only type of battery known that will operate at such a temperature, according to data presented by J. P. Schrodt, W. J. Otting, J. O. Schoegler, and D. N. Craig. Because of the potential hazard from use of perchloric acid, experimental cells containing other liquids, such as fluoboric, fluosilicic, and sulfonic acids, were also prepared. Of these, fluoboric acid gave the best results, although it is not as satisfactory as perchloric acid.

The primary purpose of this work was to produce a lightweight battery for low-temperature applications such as the radiosonde and pilot balloons for wind-direction observations. Radiosonde batteries of this type have been constructed that weigh less than 1 pound, and that have a watt-hour capacity per unit weight at room temperature almost twice that of comparable dry batteries. At lower temperatures the difference in performance is even more pronounced.

The perchloric acid battery differs from the storage battery in that the lead salts formed during discharge are freely soluble in the electrolyte, and therefore most of the active material, lead dioxide, is utilized.

The cells are designed so that the electrolyte can be introduced readily before placing them in service, and after the electrolyte has been added they can be discharged immediately without penalizing their performance. The cells can be stored indefinitely in the dry or inactivated state without special precautions against deterioration.

Plastic Coating Protects Dry Cells

A vinyl-resin plastic coating approximately 1 mm thick will protect dry batteries from deterioration and extend their shelf life at 130° F. for periods up to 6 months, as shown in accelerated tests conducted by W. J. Hamer, J. P. Schrodt, and G. W. Vinal. Storage in glass, copper cans, and metal-lined bags increased shelf life slightly, but batteries sealed in glass without venting relief built up such pressures that they exploded. At this temperature unprotected batteries were unserviceable at the end of 2 months.

Ordinarily dry cells are stored at moderate temperatures (68° to 78° F.), but during the war batteries were shipped and stored at temperatures that in some cases reached 130° F. Under these conditions batteries deteriorated rapidly, and this study was undertaken to ascertain the reasons for the deterioration and to provide means for preventing it. BA–38 dry batteries, "D-size" flashlight cells, and sections of buoy batteries consisting of "J-size" cells were used for these tests.

At 130° F. all of the batteries were found to gas with evolution of hydrogen. Samples of the gas were withdrawn at intervals and analyzed with the mass spectrometer, a procedure that permitted of hundreds of analyses that could not otherwise have been made. Composition of the gas samples indicated the process taking place within the containers, as follows: (1) In copper cans and metal-lined bags, the gas is essentially air because leaks develop in the containers as the pressure builds up within them; (2) the gas in glass apparatus eventually becomes pure hydrogen; (3) the gas in plastic containers approaches an equilibrium composition, because of the permeability of the plastic to gases. In other words, the permeability of the plastic permits escape of some of the gas formed, and access to air and water vapor—the batteries may literally "breathe." Other data indicate that drying out of the batteries and possibly the oxygen content of the surrounding gas contribute largely to the rapid deterioration of dry batteries at elevated temperatures.

Silver Peroxide-Zinc Primary Cell Gives High Output

A silver peroxide cell that produces approximately twice the output of a similar cell using monovalent silver (oxide or salt) also possesses a very constant-voltage characteristic, according to a report by I. A. Denison.

Cells containing silver-peroxide positives and zinc negatives, with an alkaline electrolyte, were discharged at both high and low rates. Even at the high rate of 2 amperes per square inch of surface, the cell voltage remained constant throughout discharge. Cells designed for low current drain delivered approximately 80 percent of their theoretical capacity.

Although silver oxides are appreciably soluble in alkali, and hence are readily reduced on coming in contact with zinc, cells were constructed that retained the greater part of their capacity during storage for 2 months at 54° C. This was accomplished by the use of asbestos as a separator. However, for best results this type of battery should be filled just prior to use.

Poisson's Ratio of Structural Alloys Determined Under Large Tensile Strains

Metals under load exhibit characteristic elastic properties up to a certain point; higher stresses produce plastic properties. Metals used in structures are generally under such loads that they behave elastically. However, as more exact knowledge of the properties of materials has become available, factors of safety have been decreased, and higher stresses, leading into the plastic range, have come into use. This requires further study, then, of the plastic properties of metals and their behavior in this range.

Among the properties on which very little data are available, for any materials, is the relation between stretch of the metal and the accompanying lateral con-

traction, known as Poisson's ratio. Methods for finding these values in the elastic range and in the plastic range, for stretches up to 18 percent, are described in the October Journal of Research (RP1742). Developed by Ambrose H. Stang, Martin Greenspan, and Sanford B. Newman, of the Bureau's Engineering Mechanics Laboratory, they have been applied to some aluminum alloys and structural steels, and these results are also reported in the paper.

The values of axial stretch versus Poisson's ratio, and axial stretch versus tensile stress, for more than 100 specimens were obtained. The materials investigated were sheets of aluminum alloy 24ST and 24SRT, of various thicknesses up to 0.125 in.; chrome-molybdenum steel 0.25 in. thick; and structural steels from 0.375 in. to 1.5 in. in thickness. Considerable variation was noted in the values of Poisson's ratio for the same stretch of nominally identical specimens.

It was found that the value of Poisson's ratio increased rapidly from its value under elastic conditions, after the proportional limit had been passed, to a maximum at a stretch of from 3 to 6 percent, and then gradually decreased as the strain was increased. The maximum value was always definitely less than one-half the value predicated on purely plastic conditions. The increase in volume due to tensile load was also calculated from some of the test results. It was found that the volume continued to increase with stretch, within the limits of the test, and did not become constant as is to be expected for purely plastic materials.

These data will also be useful when strain analyses are made of the materials which have been subjected to two-dimensional stress conditions in the plastic range. The use of actual rather than assumed values for the strains in different directions should contribute evidence toward the validity of the various theories of strength of metals.

Volume Changes in Concrete During Freezing and Thawing Observed by New Dilatometric Method

Moist concrete, when cooled slowly below the freezing point of water (32° F), may reach temperatures as low as 21.5° F before the water within the concrete freezes, but this supercooling is followed by abrupt increases in volume and temperature, as shown by recent investigations at the Bureau.

Concrete exposed to weather and to low temperatures is subject to damage by freezing and thawing; this damage is due in part to volume changes that take place during the process. In order to determine the effects of the rates of freezing and thawing upon the volume changes (transient and permanent) of concrete, a method has been devised by Rudolph C. Valore, Jr., of the Concreting Materials Section, for making continuous observations of the volume changes, the first time that such a method has been successfully used in research on concrete.

In this method, volume changes are indicated by the displacement of mercury from a steel dilatometer into a burette graduated in hundredths of a milliliter. The cylindrical test specimen (2 by 7.25 in.), with a thermoelement at its center, is sealed into the dilatometer, and the entire assembly immersed in a liquid bath in which the temperature cycle of +40° to −20° to +40° F is traversed at various rates.

For air-dried concrete specimens the volume changes were found to be uniformly linear and independent of the rate of temperature change. Coefficients of linear thermal expansion of 6.0×10^{-6}/deg F were indicated for a concrete containing siliceous sand and 3/8-in. gravel, and six bags of portland cement per cubic yard of concrete.

In moist specimens of the same composition, departures from the linear volume-temperature relationship were ascribed to freezing or thawing of water within the capillary structure of the concrete. The contraction of a specimen during cooling was interrupted as the water froze, and expansion during heating was retarded as ice melted.

When cooled slowly (10° F or less per hr), moist specimens showed uniform contraction to temperatures as low as 21.5° F, or 10° F below the normal freezing point of the water in the concrete. Following this apparent supercooling effect there was an abrupt increase in volume and temperature as water within the specimen began to freeze. When the temperature was gradually lowered after freezing had begun, the specimen again contracted uniformly, but at a greater rate than before freezing. In most cases the total contraction during the slow cooling from +40° to −20° F was greater for the moist than for the air-dried specimens, despite the abrupt increase in volume of the moist specimens as freezing began.

The magnitude of this increase depended mainly upon the degree of moisture saturation of the concrete, the extent to which the specimen had been weakened by previous freezings, and the temperature to which the water in the specimen could be supercooled before freezing. It was found that the degree of supercooling could be controlled by varying the period of time between freezing and thawing cycles during which the specimen remained unfrozen. Supercooling was virtually eliminated when this "recovery" time before a cycle was reduced to a minimum, but it was at a maximum when this time exceeded 100 hours.

During the fastest cooling, +40° to −20° F. in 30 minutes, moist specimens showed smaller amounts of contraction than during the slow cooling. These contractions became smaller as the specimen was weakened with each succeeding fast cycle. In addition, a rapidly cooled specimen maintained at −20° F. showed shrinkage lasting for several days before reaching constant volume, whereas, when cooled sufficiently slowly,

the specimen volume at any temperature during a given cycle was an irreducible minimum.

The volume of a moist specimen was usually greater at the end of a cycle of freezing and thawing than at the start. The amount of this residual expansion for each cycle varied directly with the rate of cooling, the degree of supercooling, the number of cycles previously undergone by the specimen, and the degree of saturation of the concrete. The residual expansion varied inversely with the rate of thawing.

On the basis of residual expansions, the combination of the fastest freezing and the slowest thawing appeared to be most destructive; and the slowest freezing (with a minimum of supercooling) combined with the fastest thawing, the least destructive of the treatments to which these specimens were subjected.

No attempt was made to analyze stresses on the basis of transient volume changes and elastic properties for moist specimens as stresses so computed would be, in some cases, several times greater than the nominal tensile strength of the concrete.

Proposed Simplified Practice Recommendation for Pallets

Soon to be submitted to all at interest for their consideration and adoption is a proposed Simplified Practice Recommendation for pallets for the warehousing and shipping of groceries and packaged merchandise. This recommendation is the outgrowth of a desire by members of the grocery industry to modernize their materials handling methods, and is in harmony with the nation-wide surge of interest in efficient mass distribution to match mass-production. Great impetus has been given by the war-time experience of the armed forces in the storage and shipment of vast supplies of all kinds of goods.

On August 16, 1944, at the Department of Commerce, the first conference was held for the purpose of considering the feasibility of establishing a simplified list of pallet sizes for packaged merchandise in wholesale quantities. The conference was attended by representatives of industry, the Association of American Railroads, the American Trucking Association, the American Warehousemen's Association, the U. S. Armed Services, and several bureaus of the Department of Commerce.

Committees were subsequently appointed representing the various interests, groceries processing and distribution, railroading and trucking, warehousing and materials handling equipment. Careful study covering almost 100 sizes of pallets listed in sample surveys, and involving the conduct of extensive loading and shipping tests, narrowed the list to 2 sizes that were approved at a general conference of all interests held at the National Bureau of Standards under the auspices of the Division of Simplified Practice on August 15, 1946, two years after the preliminary conference at the Department of Commerce on August 16, 1944.

The two sizes selected, 40 by 32 inches, two-way or preferably four-way, for equipment capacity of 2,000 pounds or less; and 48 by 40 in., four-way, for equipment capacity of 3,000 pounds or more, are intended to provide for as large unit loads as are feasible for the several types of warehouses and for shipping intact from the processor's plant to the distributor's order assembly line, and thus to eliminate the avoidable waste inherent in piecemeal handling and rehandling of individual packages. Adaptability is believed to have been achieved in these two sizes, to highway truck and railway freight car dimensions as well as warehouse requirements and sizes of containers which carry a major proportion of food tonnage. Besides size, the recommendation specifies the minimum vertical clearance for lift-fork entry, 3⅝ inches, and defines an approved terminology.

This initial move by the grocery industry is expected to extend its benefits and influence to other industries in their efforts toward simplified materials handling methods.

Electrode Function (pH Response) of Potash-Silica Glasses

A study of the electrode function (pH response) of a limited series of potash-silica glasses indicates voltage departures from the theoretical, at pH values greater than 4.0, of such magnitude as to render them unsuitable for glass electrodes, according to a report in the October Journal of Research (RP1743). Furthermore, results of the investigation support the theory that glasses of high hygroscopicity (water sorption) will have sensitive pH responses, and that changes in the durability of a glass will be accompanied by voltage departures for an electrode prepared from such a glass.

These two properties, namely, hygroscopicity and chemical durability in solutions of a wide range of pH values, appear to determine largely the suitability of a glass for measuring the hydrogen-ion activity of aqueous solutions, in accord with the simplified Nernst equation, $E = 0.000198T$ pH. This equation yields a theoretical value of 59 millivolts per pH at 25° C.

Five potash-silica (K_2O-SiO_2) glasses were used in this investigation by Donald Hubbard, which included determinations of hygroscopicity, pH response, and chemical durability. These glasses had been carefully prepared in the Bureau's Glass Section for studying their physical properties. Their composition varied from 71.83 to 83.07 percent of SiO_2.

The glass electrodes were blown as thin-walled tubes on the end of tubing made from the experimental glasses, and the inner electrical connection was ob-

tained by filling the bulb with mercury. Chemical durability measurements were made by the interferometer method, on a single specimen of glass that was reground and repolished after each test. In order to have results comparable with work previously reported in other publications, the Britton-Robinson universal buffer solutions were used.

All the glasses investigated showed a very high hygroscopicity, with an accompanying sensitive pH response. However, between pH 2 and 4, glasses of 71.8 and 73.6 percent SiO_2 gave pH-response values higher than the 59 millivolts per pH predicted from the Nernst equation. Electrodes prepared from all of the specimens demonstrated large voltage departures from the straight line relation with increasing alkalinity of the buffer solutions.

For a glass of 75.76 percent SiO_2 content, the voltage departures were compared with the sodium-ion concentration, $[Na^+]$, of the buffer solution, as well as with the chemical durability of the glass. The voltage departures correlated with the magnitude of the attack more convincingly than with pNa.

Although their hygroscopicity is high, giving them a very sensitive pH-response, the durability characteristics of these potash-silica glasses are so poor that voltage departures appear at pH values greater than 4.0, even for the best glass examined.

Effect of Neutral Salts On *p*-Phenol-sulfonate Buffer Solutions

Neutral salts of primary, secondary, and tertiary valences produce salt effects in buffer solutions that are independent of the specific salt used but are a function of the ion concentration and the valence type, it is reported in the October Journal of Research (RP1746).

Close control of hydrogen-ion concentration, or pH, is essential in many industrial and laboratory processes, and buffer solutions play an important part in pH measurements. Industrial solutions frequently contain various neutral salts present as byproducts or incidental to manufacture. These salts do not enter into the reaction for the electromotive force of the cell for measuring pH, but may, however, interfere with pH measurements through their effect on the buffer solutions, the so-called salt effect.

The addition of neutral salts will lower the pH of most buffer solutions. In general, the change in pH appears to result from the influence of the added salt on the activity coefficients of the buffer salts. Little information is available, however, on the magnitude of these salt effects.

In this paper Roger G. Bates, Pauline T. Diamond, Murray Eden, and S. F. Acree, of the Bureau's Section on pH Standards, describe an investigation of the effects of three salts of different valence types on the activity coefficients of the components of the dibasic *p*-phenol-sulfonate buffers. These buffers were chosen for this study because of their convenient pH range.

Three series of buffer solutions were studied by electromotive-force methods at intervals of 5 degrees from 0° to 60° C. Each solution contained equal molal amounts of potassium *p*-phenol-sulfonate and potassium sodium *p*-phenolate sulfonate. One series of solutions contained potassium nitrate, the second contained sodium sulfate, and the third trisodium citrate. The activity coefficients of buffers with and without added salt were determined at 0° to 35° C.

No pronounced differences in character were observed among the effects of salts of the different valence types in concentrations sufficient to make up one-fifth of the ionic strength of the mixture. The magnitude of the change produced by each of the three salts was found to be primarily a function of ionic strength and to be substantially unaffected by differences in the type of salt added.

Procedure Outlined for Sealing Standard Samples of Hydrocarbons "In Vacuum"

The process used by the Bureau's Hydrocarbon Standard Samples Laboratory for transferring the NBS Standard Samples of hydrocarbons to ampoules involves transfer through the vapor phase at room temperature, and sealing "in vacuum." The apparatus and procedure is described by Beveridge J. Mair, Domenic J. Termini, Charles B. Willingham, and Frederick D. Rossini, in the October Journal of Research (RP1744). The authors also describe the purification of the first 19 hydrocarbons that were made available in the series.

The apparatus consists essentially of a group of reservoirs (500-ml capacity) with side arms for filling, connected by stopcocks with one or more groups of filling tubes. The empty ampoules are attached through a glass seal to the filling tubes. The manifold system with its accessory parts can be completely sealed and, during operation, is evacuated to a pressure of 0.0001 mm Hg or lower. Vacuum pumps and gage, a source of compressed air, and suitable refrigerants, depending upon the nature of the hydrocarbons, are also provided.

After the apparatus has been cleaned thoroughly and ampoules of the desired size and type sealed to the connecting tubes, the entire system is evacuated, tested for tightness, and all leaks sealed. The hydrocarbon is then introduced into the reservoirs, and degassed by several cycles of freezing, evacuation, and melting.

In order to transfer the hydrocarbon to the individual ampoules, the reservoir is surrounded with water at room temperature and the hydrocarbon passes as vapor from the reservoir to the ampoule. Here it is collected

by cooling the ampoule with an appropriate refrigerant. When the desired quantity of hydrocarbon has been collected the ampoule is sealed off, and the process is repeated until all have been filled.

This apparatus and procedure are satisfactory for hydrocarbons having normal boiling points below about 170° C and freezing points below room temperature. The rate of transfer through the vapor phase at room temperature of hydrocarbons normally boiling above this temperature becomes impracticably slow, however, and a different apparatus has been designed for such hydrocarbons, with freezing points either below or above room temperature.

Six of the compounds were purified by regular distillation and ten by both regular distillation and azeotropic distillation. Benzene and *p*-xylene were subjected to crystallization and regular distillation, and *m*-xylene was purified by sulfonation and hydrolysis prior to the final distillation.

F. W. Smither, Chemist, Retires

Frederick W. Smither, chemist, authority on the analysis of soaps and other detergents, and chief of the Bureau's section on Detergents and Miscellaneous Materials since 1924, retired on August 31 after 39 years of continuous Government service. Mr. Smither joined the staff of the Chemistry Division in 1914, and from 1917 to 1924 was chief of the Section on Platinum Metals and Chemical Reagents.

As chairman of the Technical Committee on Detergents of the Federal Specifications Board, a position he held continuously since he organized the committee in 1921, Mr. Smither was responsible for the preparation and revision of a large number of specifications used in Government procurement operations. He also organized and served as chairman of the Board's Technical Committee on Fire Extinguishing Liquid, and has been a member of the committees on chemical products, laundry equipment, and floor treatments.

Mr. Smither has been a member of the Editorial Advisory Board for the journal Oil and Soap since 1939. He has published papers on the performance of glass and platinum laboratory ware, on detergents, the analysis of paints, and other subjects. Mr. Smither is author of the popular Bureau Circular on washing, cleaning, and polishing materials, which has been through several revisions.

Mr. Smither has served on committees for the analysis of soap and other detergents of the American Chemical Society, as chairman since 1937; of the American Society for Testing Materials, as vice chairman of Committee D–12 since the committee was organized in 1936; and of the American Oil Chemists Society (1926–46). Mr. Smither was president of the Chemical Society of Washington in 1926, and is a fellow of the American Association for the Advancement of Science.

A native of Hampton, Va., Mr. Smither received the B. S. degree at Virginia Polytechnic Institute in 1895 and followed this with two years of graduate study at the University of Virginia. In addition to several years with industrial chemical laboratories, he was associated with the Department of Agriculture before coming to the National Bureau of Standards.

New and Revised Publications Issued During September 1946

Journal of Research [1]

Journal of Research of the National Bureau of Standards, volume 37, number 2, August 1946 (RP1730 to RP1735, inclusive). Price 30 cents. Annual subscription, 12 issues, $3.50.

Circulars [1]

C452. Slip casting of clay pots for the manufacture of optical glass at the National Bureau of Standards. Raymond A. Heindl, Gordon B. Massengale, and Louis G. Cossette. Price 10 cents.

C454. Proving rings for calibrating testing machines. Bruce L. Wilson, Douglas R. Tate, and George Borkowski. Price 10 cents.

Simplified Practice Recommendation [1]

R218–46. Paper tubes for packaging milk-bottle caps. Price 5 cents.

Building Materials and Structures Report [1]

(Persons who wish to be notified of new publications in the Building Materials and Structures series as soon as they are available should write to the Superintendent of Documents, Government Printing Office, Washington 25, D. C., asking that their names be placed on the special mailing list maintained for this purpose.)

BMS106. Laboratory observations of condensation in wall specimens. Richard S. Dill and Herman V. Cottony. Price 10 cents.

Basic Radio Propagation Predictions [1]

CRPL–D25. Basic radio propagation predictions for December 1946 three months in advance. Issued September 1946. Price 15 cents. Annual subscription, 12 issues, $1.50.

Technical News Bulletin [1]

Technical News Bulletin 353, September 1946. Price 5 cents. Annual subscription, 12 issues, 50 cents.

Mimeographed Material

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LC826. Simplified practice recommendations. Alphabetical list revised to July 1, 1946. (Supersedes LC816)

LC827. Sunlamps, therapeutic lamps; ultraviolet and infrared lamps. (Supersedes LC631)

LC829. House plan services. (Supersedes LC801)

LC830. List of published material relating to home building and maintenance. (Supersedes LC805)

[1] Send orders for publications under this heading only to the Superintendent of Documents, Government Printing Office, Washington 25, D. C. Subscription to Technical News Bulletin, 50 cents a year; Journal of Research, $3.50 a year (to addresses in the United States and its possessions and to countries extending the franking privilege); other countries, 70 cents and $4.50, respectively. The price of other publications is indicated in the lists.

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